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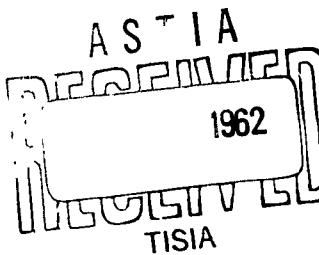


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TERNARY MINERALS AND COMPOUNDS:  
AN ANNOTATED BIBLIOGRAPHY

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FEBRUARY 1962

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## TERNARY MINERALS AND COMPOUNDS: AN ANNOTATED BIBLIOGRAPHY

Compiled by  
A.A.BELTRAN

SPECIAL BIBLIOGRAPHY  
SB-62-4

FEBRUARY 1962

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## ABSTRACT

This annotated bibliography is concerned with ternary minerals and compounds of metallic elements with Group V metalloids and Group VI nonmetallics (selenides, sulfides and tellurides). The literature primarily covers the period from 1959 to 1961. However, thesis from as early as 1947 and a few Russian articles from 1955 have been included.

Search completed January 1962.

## INTRODUCTION

The literature search, from which this annotated bibliography resulted, was concerned primarily with ternary minerals as they occurred in nature. Literature on ternary compounds has been included for comparison. The search was concentrated over the three year period from 1959 through 1961. However, applicable thesis from as early as 1947, and a few continuing Russian articles from 1955 have been included.

Reports and articles on the properties of ternary minerals and compounds of the following elements are presented.

Metallic Elements

	<u>Group V Metalloids</u>	<u>Group VI Nonmetallics</u>
Cobalt (VIII)		
Copper (Ib)		
Iron (VIII)	Antimony	Selenium
Lead (IVb)	Arsenic	Sulfur
Manganese (VIIa)	Bismuth	Tellurium
Mercury (IIb)		
Nickel (VIII)		
Silver (I)		
Thallium (III)		
Zinc (II)		

An excellent source of information on ternary minerals, not listed in this bibliography is:

Dana, James D.  
MANUAL OF MINERALOGY. 17th ed., rev.  
by C. S. Hurlbut, Jr. N. Y., Wiley, 1959, 609p.

In this volume one may find, for example, the following sulfides:

Arsenopyrite - - - - FeAsS	Polybasite - - - Ag <sub>16</sub> Sb <sub>2</sub> S <sub>11</sub>
Bournonite- - - - - PbCuSbS <sub>3</sub>	Proustite - - - Ag <sub>3</sub> AsS <sub>3</sub>
Chalcopyrite - - - - CuFeS <sub>2</sub>	Pyrargyrite - - Ag <sub>3</sub> SbS <sub>3</sub>
Cobaltite - - - - - (Co, Fe)AsS	Stannite- - - - Cu <sub>2</sub> FeSnS <sub>4</sub>
Enargite- - - - - Cu <sub>3</sub> AsS <sub>4</sub>	Stephanite - - - Ag <sub>5</sub> SbS <sub>4</sub>
Jamesonite - - - - - Pb <sub>4</sub> FeSb <sub>6</sub> S <sub>11</sub>	Tetrahedrite- - (Cu, Fe, Zn, Ag) <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>

The entries in the bibliography are arranged alphabetically by author. An extensive subject index makes every mineral, compound, selenide, sulfide and telluride readily available.

1.

Allgaier, R.S.

THE 1960 INTERNATIONAL CONFERENCE ON  
 SEMICONDUCTOR PHYSICS AT PRAGUE: THE  
 LEAD SALT SEMICONDUCTORS bS, PbSe, AND  
 PbTe, AND OTHER SELENIDES AND TELLURIDES.

Naval Ordnance Lab., White Oak, Md. Rept.  
 No. NAVWEPS 7332. 18 Oct 60, 9p.

ASTIA AD-252 874

Information obtained at the Prague Semiconductor Conference on the lead salts (Sulfide, Selenides, and Tellurides) from papers and personal contacts, and later, from follow-up correspondence is described. The Conference session, entitled Selenides and Tellurides, is also summarized.

2.

Armstrong, R.W., Faust, J.W. Jr. and Tiller, W.A.

A structural study of the compound AgSbTe<sub>2</sub>.  
 Westinghouse Res. Lab., J. APPL. PHYS.,  
 v. 31, p. 1954-1959, Nov 1960.

The use of x-ray, optical and electron microscope, and chemical etching techniques to investigate a striated microstructure, observed in zone refined single crystals of the AgSbTe<sub>2</sub> structure is reported. This microstructure, originally thought to be fine twin lamellas, has been identified as a Widmanstatten precipitate of Sb<sub>2</sub>Te<sub>3</sub> upon the (111) planes of the matrix face-centered cubic material. In addition, the evidence obtained from all measurements made on this material indicates that the ternary compound of the AgSbTe<sub>2</sub> does not melt congruently.

3.

Bennett, L.C. and Wiese, J.R.

Effects of doping additions on the thermoelectric conductor Bi<sub>2</sub>Te<sub>2.1</sub>Se<sub>0.9</sub>. J. APPL. PHYS.  
 (USA) v. 32, n. 4, p. 562-4, Apr 1961.

An alloy of 70 mol % Bi<sub>2</sub>Te<sub>3</sub>-30 mol % Bi<sub>2</sub>Se<sub>3</sub>, or Bi<sub>2</sub>Te<sub>2.1</sub>Se<sub>0.9</sub> is the intrinsic semiconductor of the pseudobinary system Bi<sub>2</sub>Te<sub>3</sub>-Bi<sub>2</sub>Se<sub>3</sub>. This V-VI alloy was doped with lead(Group IV) and iodine (Group VII) separately and together. The effects of

3. (Cont'd) the dopants are analogous to those produced by Group III or Group V impurities in Group IV elemental semiconductors, the lower group impurity producing a p-type material and the higher group impurity an n-type material. Plots of the Seebeck coefficient, electrical conductivity, and thermal conductivity are given as a function of impurity concentration and show that the separate effects of the impurities are countered when the impurities are in the lattice together in the same amount. Doping was also done with silver and iodine, separately and together. The results indicate that the silver is in the lattice interstitially (lead and iodine substitutionally) and that the type material produced is dependent also on how the impurity atom enters the lattice.

4.

Born, L. and Hellner, E.

A structural proposal for boulangerite. AMERICAN  
MINERALOGIST, v. 45, n. 11-12, p. 1266-71, Nov-  
Dec 60.

A structure for the sub-cell of boulangerite ( $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ ) is proposed which explains the morphology (as needles) and shows the boundary between the "galena-like" and the "stibnite-like" structures of complex sulfides.

5.

Bubyreva, N. S. and Obukhov, A. P.

Physico-chemical examination of the ternary  
system thallium-selenium-tellurium. (Fiziko-  
khimicheskoye issledovaniye troynoy sistemy tally-  
selen-tellur.) Leningrad Physico-Technical Institute  
of the Academy of Sciences, USSR. ZHURNAL  
NEORGANICHESKOI KHIMII, v. 4, n. 1, p. 132-137,  
1959. (In Russian)

The ternary system thallium-selenium-tellurium was investigated by measuring the specific conductivity, investigating the microstructure, and by thermal analysis. The synthesis of the samples was carried out by melting the chemically pure metals in evacuated vessels. For the surface construction of the liquid, 94 alloys were examined and the phase diagram was plotted. The system has no ternary eutectics nor ternary compounds. Five crystalline zones are formed. In the first crystallization zone, primary separation of tellurium and selenium takes place. In the second zone, solid solutions between  $\text{Tl}_2\text{Se}$  and  $\text{Tl}_5\text{Te}_3$  form in the third zone. The fourth crystallization zone has no solid solutions. The fifth zone probably has the compound  $\text{Tl}_2\text{Se}_3$ . The

5. (cont'd) compounds in the second crystallization zone, Tl Se and Tl Te, have analogous chemical properties and similar crystalline structures as has been proved by X-ray analysis. The composition of the phases I, II, and III corresponds to solid solutions. The alloys of the system possess semiconductor properties. The specific electric conductivity of the alloys depends considerably on the composition and it changes from  $1.10^2$  to  $1.10^{-5}$  ohm $^{-1}$  cm $^{-1}$ . The maximum conductivity of  $1.10^2$  is at the limit of metallic conductivity because these alloys contain admixtures of metallic thallium.

6. Buhrer, Carl F.

SOME PROPERTIES OF BISMUTH PEROVSKITES,  
Laboratory for Insulation Research, Mass. Inst.  
of Tech., Cambridge. Technical rept. no. 160,  
Mar 61, 26p., (Contracts AF 19(604)6155 and  
Nonr-184110). ASTIA AD-253 293.

The crystallographic and dielectric properties of complex perovskites are described in terms of average A- and B- site ionic radii, charges, electronic structures, etc. The relative importance of these to the ferroelectric state is evaluated by a study of a number of solid solutions containing trivalent bismuth. Two new ferroelectrics, Bi0.5K0.5Ti03 and Bi0.5Na0.5Ti03, and the phase diagrams of the systems BixKxBa1-2xTi03, Bi0.5KxNa0.5-xTi03, BixKxPb1-2xZr03, and BixNaxPb1-2xZr03 are reported.

7. Cosgrove, G.J., McHugh, J. P. and Tiller, W. A.  
Effect of freezing conditions on the thermoelectric  
properties of BiSbTe<sub>3</sub> crystals. J. APPL. PHYS. (USA)  
v. 32, n. 4, p. 621-3, Apr 61.

The thermoelectric parameters  $\alpha$ ,  $1/p$ , and  $1/(K-K_e)$  of oriented polycrystals increase as the freezing rate decreases and as the temperature gradient in the liquid at the interface increases. The effects are primarily attributed to the variation in the degree of micro-segregation produced in the crystals as a function of the freezing conditions.

8. Dudkin, L. D. and Ostranitsa, A. P.  
Ternary Semiconducting compounds A<sup>I</sup>B<sup>V</sup>B<sub>2</sub><sup>VI</sup>.  
DOKL. AKAD. NAUK SSSR v. 124, n. 1, p. 94-7,  
Jan 1, 1959. (In Russian)

8. (cont'd) Four compounds were studied: CuSbSe<sub>2</sub>, AgSbSe<sub>2</sub>, AgSbTe<sub>2</sub>, and AgBiSe<sub>2</sub>, with melting points at 472, 634, 561 and 792°C, respectively. (AgBiSe<sub>2</sub> showed a polymorphic transformation at 298°C). Electrical and thermal conductivity, thermo-electric power and microhardness were measured. Thermal activation energies were (in eV): AgSbSe<sub>2</sub>, 0.58; CuSbSe<sub>2</sub>, 0.16 and 0.80; AgBiSe<sub>2</sub>, 0.34 (low temperature form and 1.10 (high temperature form). A chemical bonding scheme is suggested in which A<sup>I+</sup> ions are situated in a covalently bonded (B<sup>V</sup>-B<sup>VI</sup>)<sup>-</sup> structure.

9. Earley, J. W.

DESCRIPTION AND SYNTHESIS OF THE SELENIDE  
MINERALS. Ph. D. Thesis, University of Toronto,  
1950, 87p.

This is a contribution to the pure mineralogy (natural history) of the selenides. Its primary purpose is to improve the descriptive mineralogy of the group, as given in Dana, 1944 and Klockmann - Ramdohr, 1948 by verification, correction, and extension of the specific data, and to reconsider the classification of the selenides in the larger sulphide group. To supplement observations on natural material, which was almost always extremely scanty, the corresponding pyrosynthetic compounds were in most instances successfully prepared and studied as artificial minerals.

Elagina, E. I.

see Yelagina, Ye. I.

10. Fleischmann, H., Folberth, O. G. and Pfister, H.

Semiconducting mixed crystals of the type

(A<sup>I</sup><sub>x/2</sub> B<sup>IV</sup><sub>(1-x)</sub> C<sup>V</sup><sub>x/2</sub>)D<sup>VI</sup>. Z. NATURFORSCH., v. 14a,  
n. 11, p. 999-1000, Nov 1959. (In German.)

The example investigated was (Ag<sub>x/2</sub> Pb<sub>(1-x)</sub> Bi<sub>x/2</sub>)Te and this was found to have the NaCl structure, the lattice parameter varying linearly with composition. The thermal conductivity passed through a minimum value of only 0.005 W cm<sup>-1</sup> deg<sup>-1</sup> which, associated with an electrical conductivity of 300 ohm cm, could be of interest for thermo-electric applications.

11. Frueh, A. J., Jr.  
 The crystallography of petzite,  $\text{Ag}_3\text{AuTe}_2$ .  
 AMERICAN MINERALOGIST, v. 44, n. 7-8,  
 p. 693-701, Jul-Aug 59.

From small single crystals of petzite found intimately intergrown with hessite ( $\text{Ag}_2\text{Te}$ ) from Botes, Transylvania, the space group was determined to be cubic, I4.32 with a cell edge of 10.38 Å. There are 8( $\text{Ag}_3\text{AuTe}_2$ ) per cell and the atoms are located on the following special positions: 24 silver atoms on x, 0, 1/4, etc. with x = 0.365; 8 gold atoms on 1/8, 1/8, 1/8, etc.; 16 tellurium atoms on x,x,x, etc. with x = 0.266.

12. Goryunova, N. A. and Kolomijez, B. T.  
 Glass-like semiconductors. IZVESTIYA AKADEMII  
 NAUK S.S.R., SERIYA FIZICHESKAYA, v. 20,  
 p. 1496-1500, 1956, (In Russian). English Translation  
 in Bulletin of the Academy of Sciences of the  
 U.S.S.R., Physical Series, v. 20, p. 1372-76, 1956.

Compounds lying in the following composition ranges were examined:  $\text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3$ ,  $\text{As}_2\text{Se}_3-\text{Tl}_2\text{Se}$ ,  $\text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3$ ,  $\text{As}_2\text{Se}_3-\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3 \cdot \text{Tl}_2\text{Se} \cdot \text{Sb}_2\text{Se}_3 \cdot \text{Tl}_2\text{Se}$ ,  $\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ . The ternary and quaternary systems were either crystalline or glass-like, with a well-defined composition boundary separating the two phases; however, for some composition both phases were present. The electrical and optical properties of the compounds are briefly described.

13. Goryunova, N. A. and Kolomiets, B. T.  
 Properties and structure of ternary semiconducting  
 systems. II. Electrical properties and structure  
 of materials in systems of the thallium, antimony  
 and arsenic selenides. ZH. TEKH. FIZ.,  
 v. 25, n. 12, p. 2069-78, 1955. (In Russian).

13. (cont'd) Materials in the systems  $Tl_2Se$ ,  $As_2Se_3$ - $Tl_2Se$ ,  $Sb_2Se_3$  and  $Sb_2Se_3$ - $As_2Se_3$  were prepared by direct fusion and subsequent slow cooling. All specimens were p-type semiconductors. Curves of electrical conductivity v. temperature and the corresponding activation energies are given. Evidence of glass-like amorphous structure was found for compositions rich in  $As_2Se_3$ .

14. Goryunova, N. A., Kolomiets, B. T. and Mal'kova, A. A.  
 Properties and structure of ternary  
 semiconducting systems. III.  
 Conductivity and photoconductivity in  
 systems of the thallium, antimony and  
 bismuth sulphides. ZH. TEKH. FIZ.  
 v. 26, n. 8, p. 1625-33, 1956.  
 (In Russian)

$Tl_2S$ - $Sb_2S_3$ : a marked minimum in conductivity ( $\sigma$ ) and a maximum in thermal activation energy were found near  $Tl_2S$ . $3Sb_2S_3$ . X-ray analysis showed this to be a new compound; a further compound was indicated near  $2Tl_2S$ . $Sb_2S_3$ . Substitution of As for Sb in the alloy  $Tl_2S$ . $Sb_2S_3$  shifted the peak of the photoconductive spectral response (P) to longer wavelengths.  $Bi_2S_3$ - $Sb_2S_3$ : a complete range of semiconducting solid solutions appeared to form. A minimum in  $\sigma$  was observed near 40%  $Sb_2S_3$ . Small additions of S to the 50 : 50 alloy shifted P to longer wavelengths, but larger amounts (i.e.  $Bi_2S_3$ . $Sb_2S_5$ ) gave the response of pure S.

15. Goryunova, N. A., Kolomiets, B. T. and Shilo, V P.  
 Vitreous semiconductors. IX. Vitrification  
 in complex chalcogenides based on  $As_2S_3$  and  
 $As_2Se_3$ . FIZ. TVERDOGO TELA. v. 2, n. 2,  
 p. 280-3, Feb 1960. (In Russian)

Alloys of  $As_2Se_3$  with the sulphides (or selenides) of elements of the groups Ib (Cu, Ag, Au), IIB (Zn, Cd, Hg), IIIB (Ga, In, Ti) and IVb (Ge, Sn, Pb) were prepared and the extent of vitrification in each ternary system was approximately determined. Ti and Ge showed a much larger vitrification than other elements. The results cannot be easily interpreted, but some correlation was found to exist between the heat of formation of the chalcogenides of the elements of groups I-IVb and the area of the vitrification zone.

16. Harman, T. C., Strauss, A. J. and Farrell, L. B.  
 PROPERTIES OF  $HgSe$ - $HgTe$  ALLOYS. Lincoln

16. (cont'd)

Lab. 1960 Fall Mtg. Electrochem.

Soc.

Determination of the phase diagram for the pseudo-binary system HgSe-HgTe by differential thermal analysis and x-ray diffraction techniques was reported. Melting points measured for HgSe and HgTe are 799° and 670°C, respectively. Continuous solid solution occurs over the whole range of composition. Large single crystals of the alloys have been prepared by the Bridgman method. Data on the electrical properties of the alloys as a function of composition, impurity concentration, and temperature were presented.

17.

Hockings, E. F.

The thermal conductivity of silver  
antimony telluride. RCA Laboratories.

PHYSICS AND CHEMISTRY OF SOLIDS

v. 10, n. 4, p. 341-342, Aug 1959.

The compound was prepared directly from the elements in an evacuated quartz ampule by heating to 700 C, mixing the resulting liquid by agitation, and then cooling at 5 C/min. The product was a macrocrystalline ingot with grains up to 5 mm in length and with an electrical resistivity of  $5.3 \times 10^{-3}$  Ω-cm. Thermoelectric measurements showed it to be a p-type, nondegenerate semiconductor. X-ray powder diffraction patterns showed a single-phase face-centered cubic structure with  $a = 6.076$  Å. The thermal conductivity at 300 K was determined by the standard method of placing cylindrical specimens between a heater and a heat sink. Measurements were made of the thermal gradients associated with known heat flows. The thermal conductivity of  $\text{AgSbTe}_2$  is 0.0071 W./degree-cm at 300°K. The electronic component was estimated as 0.0008 watt/degree-cm.

18.

Ibrahim, M. A.

TERNARY PHASE IN THE  $\text{M}_9\text{S}_8$  SECTION  
OF THE SYSTEM Fe-Co-Ni-S. Master  
of Engineering Thesis, Nova Scotia Technical  
College, Halifax, 1959, 85p., 44 refs.

The (Fe, Co, Ni)<sub>9</sub>S<sub>8</sub> section of the quaternary system Fe-Co-Ni-S at room temperature has been investigated by X-ray diffraction methods. The face-centered cubic pi phase, which is known from the system Co-S and from the mineral pentlandite, has been shown to exist in the quaternary system over an appreciable range of compositions. The composition of natural pentlandite is discussed as well as the reasonability of the crystal structure which has been proposed for it by Eliseev. Lattice constants of natural pentlandite from widely separated localities have been found to be closely similar to each other but lower than those of synthetic pentlandites of any composition. Prolonged heat treatment at 350-390°C raises the lattice constants of practically pure pentlandite to values comparable with the values obtained for synthetic samples. Possible reasons for this behavior are discussed.

19. Johan, Z. and Hak, J.  
 Novakit --  $(\text{Cu}, \text{Ag})_4\text{As}_3$ , ein neues  
 Mineral. CHEMIE DER ERDE v. 20,  
 p. 49-50, 1959. (In German)  
 Analysis (mean of 2) gave Cu 41.39, As 43.30, Fe 5.13, Ag 1.96, Co 0.79, S 2.73, CaO 2.72, CO<sub>2</sub> 2.13 for a total of 100.15%. After deducting calcite, S as chalcocite, and Fe as loelfingite, and recalculation to 100 yields As 45.82, Cu 50.91, Ag 3.27%. This corresponds to  $(\text{Cu}, \text{Ag})_{1.36}\text{As}$  or  $(\text{Cu}, \text{Ag})_4\text{As}$  or  $(\text{Cu}, \text{Ag})_{11}\text{As}_8$ .

30. Kokosh, G. V. and Sinani, S. S.  
 Thermoelectric properties of alloys of the  
 pseudobinary system  $\text{Sb}_2\text{Te}_3\text{-Bi}_2\text{Te}_3$ .  
 Leningrad Inst. Semicon. SOVIET PHYS. -  
 SOLID STATE v. 2, p. 1012-1018, Dec 1960.  
 The effect of impurities on the properties of alloys of the system  $\text{Sb}_2\text{Te}_3\text{-Bi}_2\text{Te}_3$  is considered. A general description of the effect of additions on solid solutions of semiconductors with disturbed stoichiometry is presented. The effect of firing on the electrical conductivity and thermal EMF of pressed specimens is described. The properties of alloys made of materials of different purity are compared. The part of the system exhibiting maximum values of the thermal EMF is examined.

21. Kolomiets, B. T. and Nazarova, T. F.  
 The effect of impurities on electrical  
 conduction in vitreous  $\text{As}_2\text{SeTe}_2$ . FIZ.  
 TVERDOGO TELA. v. 2, n. 1, p. 174-6,  
 Jan 1960. (In Russian)  
 Zone purification of  $\text{As}_2\text{SeTe}_2$  ( $\text{As}_2\text{Se}_3\text{-}2\text{As}_2\text{Te}_3$ ) left the electrical conductivity ( $\sigma$ ) of a vitreous material practically unaffected ( $\sim 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ , p-type) but lowered considerable  $\sigma$  of crystals (it fell from 60 to  $\sim 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) and altered it from p- to n-type. This suggests that impurity conduction is important in crystals but not in vitreous material.

22. Kolomiets, B. T. and Pozdnev, V. P.  
 Glassy semiconductors. VII. Viscosity  
 of vitreous semiconductors in the  $\text{As}_2\text{Se}_3\text{-}$   
 $\text{As}_2\text{Te}_3$  system. FIZ. TVERDOGO TELA.  
 v. 2, n. 1, p. 28-34, Jan 1960. (In Russian)

Compositions between  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Se}_3\text{As}_2\text{Te}_3$  were studied (400-800°C) by a rotational method. Kinematic viscosity ( $\nu$ ) decreased smoothly with  $\text{As}_2\text{Te}_3$

22-1 (cont'd) concentration (x) and with temperature (at ~400°C it varied from ~ $10^2$  to  $10^{-1}$  stokes; at ~700°C from ~10-1 to 10-2 stokes). Activation energies (E) for viscous flow were evaluated (24.3-21.8 kcal/mole, decreasing with increasing x) as were the corresponding entropies of activation (in the range +7.2-8.75 cal/deg. mole). This behaviour was interpreted in terms of a chain structure: the low softening temperatures (< 200°C) were ascribed to the breaking of interchain Van der Waals bonds, and the constant E for a given composition to the breaking of intrachain covalent bonds.

23. Kolomiets, B. T. and Nazarova, T. F.

Hall effect in vitreous materials of the  
 $Tl_2Se \cdot As_2(Se, Te)_3$  system. Phys. Tech.  
 Inst., Leningrad. FIZ. TVERDOGO TELA.  
 v. 2, p. 395-6, 1960. (In Russian)

The Hall mobility was measured at room temp. as a function of Te content. The mobility remained const. at  $10^{-2}$  sq. cm./v.-sec. for all compns., although the carrier concn. increased linearly from  $10^{11}$  to  $10^{18}$ /cc. as the compn. was varied from  $Tl_2Se \cdot As_2Se_3$  to  $Tl_2Se \cdot As_2Te_3$ .

24. Kolomiets, B. T. and Goryunova, N. A.

Properties and structure of ternary  
 semiconducting systems. I. Electrical  
 properties and structure of some materials  
 in the system Tl-Sb-Se. ZH. TEKH. FIZ.  
 v. 25, n. 6, p. 984-94, 1955. (In Russian)

Alloys between  $Tl_2Se$  and  $Sb_2Se_3$  were prepared by direct fusion and slow cooling. All were p-type semiconductors. Thermoelectric power, electrical conductivity, Hall effect and photoconductive spectral response were studied and evidence was obtained of the formation of a compound  $Tl_2Se \cdot Sb_2Se_3$  (rhombic a = 4.15, b = 4.50, c = 12.0 Å). Preliminary work on alloys of  $Tl_2Se$  with  $As_2Se_3$  and  $As_2Te_3$  is reported. Amorphous glass-like materials were observed.

25. Kolomiets, B. T. and Lyubin, V. M.

Properties and structure of ternary  
 semiconductor systems. VI. Electrical  
 and photoelectric properties of  $Sb_2S_3$ -  
 $Bi_2S_3$  layers. FIZ. TVERDOGO TELA.  
 v. 1, n. 5, p. 740-7, May 1959.  
 (In Russian)

The layers (0.5-4 $\mu$  thick) were prepared by evaporation in vacuo. Their V-I characteristics (Ohm's law was obeyed), dark resistance at temperatures from room

25. (cont'd) to 400° C, and spectral distribution of photoconductivity were recorded. It was found that heating to temperatures above 200-220° C reduces the resistance of the layers irreversibly by a factor of 2-3 and makes them opaque.

26.

Kolomiets, B. T. and Nazarova, T. F.

The role of impurity in the conductivity of vitreous  $\text{As}_2\text{-SeTe}_2$ . Phys. Tech. Inst., Leningrad. FIZ. TVERDOGO TELA v. 2, p. 174-6, 1960. (In Russian)

The elec. cond. of cryst. and vitreous  $\text{As}_2\text{SeTe}_2$  were measured after synthesis and various zone refining techniques. The cond. of the cryst. material varied between 0.04 and 60 ohm<sup>-1</sup> cm. whereas the vitreous samples were quite insensitive to the method of prepn. (elec. 10<sup>-6</sup> ohm<sup>-1</sup> cm.<sup>1</sup>). The temp. dependence of the cond. for both modifications was presented graphically between 170° and 500°K.

27.

Kolomiets, B. T. and Ling, Ch'ung-Ming  
Spectral distribution of the internal  
photoelectric effect in the ZnSe-CdSe system.  
Phys.-Tech. Inst., Acad. Sci. U.S.S.R.,  
Leningrad. FIZ. TVERDOGO TELA v. 2,  
p. 168-70, 1960. (In Russian)

The spectral distribution of the internal photoelec. effect and the lattice parameters of the Zn<sub>x</sub>Cd<sub>1-x</sub>Se system were measured. x took on the values 0, 0.2, 0.25, 0.33, 0.50, 0.67, 0.75, 0.8, and 1.0. Although the lattice type changed from wurtzite to sphalerite for 0.3 < x < 0.5, the band gap varied smoothly ( a neg. deviation from linearity) across the entire system. The effect of replacing Cd with Zn upon the shape of the spectral distribution was discussed.

28.

Kolomiets, B. T. and Pavlov, B. V.  
Vitreous semiconductors. VIII. Optical  
properties of glasses based on the chalco-  
genides of thallium, arsenic and antimony.  
FIZ. TVERDOGO TELA v. 2, n. 4,  
p. 637-43, Apr 1960. (In Russian)

Optical absorption spectra were studied between 0.5 and 18  $\mu$  for various compositions in the systems:  $\text{As}_2\text{S}_3\text{-As}_2\text{Se}_3$ ,  $\text{As}_2\text{S}_3\text{-As}_2\text{Te}_3$ ,  $\text{As}_2\text{Se}_3\text{-As}_2\text{Te}_3$ ,  $\text{As}_2\text{Se}_3\text{-Tl}_2\text{Se}$ ,  $\text{As}_2\text{S}_3\text{-Tl}_2\text{S}$ , and  $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3$ . Two more complex compositions:  $\text{Tl}_2(\text{Te}_{0.5}\text{Se}_{0.5})$ ,  $\text{As}_2\text{Te}_3$  and  $\text{Tl}_2\text{Se.3Tl}_2\text{Te.3As}_2\text{Se}_3\text{.3As}_2\text{Te}_3$ , with main absorption edges,  $\lambda_{G'}$  at 2.07 and 3.50  $\mu$  respectively, were also studied. Optical absorption beyond the main edge

28. (cont'd) was low for most glasses studied ( $0.5\text{--}1.0 \text{ cm}^{-1}$ ), and it is suggested that optical filters for the range  $0.6\text{--}3.0 \mu$  could be made by combining glasses with appropriate  $\lambda_G$ . Plots of numerous absorption spectra are presented. It is noted that polished sections cut from ingots and hot pressed discs gave almost identical plots.

29. Kostov, I.  
 Bismuth jamesonite or sakharovite -- a  
 new mineral species. TRUDY  
 MINERALOGICHESKOGO MUZEYA AKADEMII  
 NAUK S. S. S. R. v. 10, p. 148-9, 1959.  
 (In Russian)

A mineral called bismuth jamesonite was described by M. S. Sakharova in 1955 (AMER. MINERAL v. 41, p. 814, 1956) with the formula  $\text{Pb}(\text{Sb}, \text{Bi})_2\text{S}_4$ , with a 1 to 1 ratio of Sb to Bi. No new data are given; Kostov considers the mineral to be a new species and suggests the name sakharovite.

30. Kouvo, O., Huhma, M. and Vuorelainen, Y.  
 A natural cobalt analogue of pentlandite.  
 AMERICAN MINERALOGIST v. 44, n. 7-8,  
 p. 897-900, July-Aug 1959.

The pentlandite of Varislahti (Finland), Savonranta pyrrhotite deposits, and the pyrrhotite of the Outokumpu mine are described. These pentlandites, rich in cobalt, are associated with copper and iron sulfides.

31. Kupeik, V., Matherney, M. and Varcek, C.  
 The problem of the structure of the mineral  
 "lillianite." GEOLOGICHESKII SBORNIK  
 (BRATISLAVA) v. 12, p. 103-13, 1961.  
 (In Czechoslovakian)

Microchemical and spectrographic analysis of a mineral from Aurelia gave Pb 45.78 and Bi 28.32%, corresponding to the formula  $\text{Pb}_3\text{Bi}_2\text{S}_6$ . X-ray powder data are compared with those for cosalite, galenobismutite and kobellite; those for the mineral lead to a unit cell a  $4.10 \pm 0.01$ , b  $15.84 \pm 0.03$ , and c  $19.02 \pm 0.04 \text{ kX}$ ; space group is Pbnm (?), Z = 4, d. (measured) 7.10, and d. (calculated) 6.58.

32. Lowther, H. C.  
 THE APPLICATION OF POLARIZATION  
 FIGURES AND ROTATION PROPERTIES

32. (cont'd)

TO THE IDENTIFICATION OF CERTAIN  
OF THE LEAD SULPHANTIMONIDES.  
M. S. Thesis in Geology, University of  
Wisconsin, 1952.

33.

McHugh, J. P., Cosgrove, G. J. and Tiller, W. A.  
THE EFFECT OF FREEZING CONDITIONS  
ON THE THERMOELECTRIC PROPERTIES  
OF  $\text{BiSbTe}_3$  CRYSTALS. Westinghouse Res.  
Labs. 1961 Symp. Thermoelectric Energy  
Conversion.

An investigation of the effects of growth rate and interface temperature gradient on the thermoelectric parameters  $\alpha$ ,  $1/p$  and  $1/(K - K_e)$  using Bridgman grown, oriented polycrystals of  $\text{BiSbTe}_3$  was discussed. All four parameters were found to increase as the freezing rate decreases and the temperature gradient in the liquid at the interface increases. The effects are primarily attributed to the variation in the degree of micro-segregation produced in the crystals by the freezing condition.

34.

Mason, D. R. and O'Kane, D. F.  
Preparation and properties of some  
peritectic semiconducting compounds.  
U. of Michigan. J. ELECTROCHEM.  
SOC. v. 107, p. 268C, Dec 1960.

Preliminary results on the preparation and properties of ternary semiconducting compounds in the homologous series  $1_{1-\beta} \text{InV}_{\beta}$  and  $11_{1-\beta} \text{In}_2 \text{V}_{1+\beta}$  were presented. These ternary compounds represent a linear combination of two binary constituents, each of which has semiconducting properties. One constituent can be represented by the chemical formula  $111_{2-\beta} \text{V}_{1+\beta}$  and the other constituent either as  $1_{2-\beta} \text{V}_{1+\beta}$  or as  $11_{2-\beta} \text{V}_{1+\beta}$ . Since each of the binary constituents is a pure chemical component, adequate equilibrium relationships can be obtained by investigating only the pseudobinary plane which joins them in the ternary system. A redetermination of the melting points and phase diagrams of some of the binary constituents has been undertaken in order to correct several serious inaccuracies in the literature. The determination of the phase diagrams for the various pseudobinary systems is in progress, using differential thermal analysis, and microscopic and x-ray examinations. It has been found that  $\text{HgIn}_2\text{Te}_4$  is the only compound in either series that is definitely known to be congruently melting; the remaining nine compounds appear to be peritectics. The system  $\text{CdTe}-\text{In}_2\text{Te}_3$  has been characterized quite completely, and homogeneous samples of the peritectic compounds in this system have been prepared using zone refining techniques.

35. Milton, C. and Ingram, B.  
 Note on "revoredite" and related lead-sulfur-arsenic glasses. AMERICAN MINERALOGIST v. 44, n. 9-10, p. 1070-76, Sep-Oct 1959.

Revoredite from Cerro de Pasco, Peru consists of lead, arsenic, and sulfur, and is amorphous to X-rays. Another deposit consisting of  $\text{As}_2\text{S}_3\text{-}2\text{PbS}$  from Quiruvilca, Peru was studied. Lead sulfarsenides similar to "revoredite" have also been found in Wiesloch, Baden, Germany.

36. Miyatani, Shin-ya  
 Electrical properties of pseudo-binary systems of Ag VI's;  $\text{Ag}_2\text{Te}_{\underline{x}}\text{Se}_{1-\underline{x}}$ ,  $\text{Ag}_2\text{Te}_{\underline{x}}\text{S}_{1-\underline{x}}$ , and  $\text{Ag}_2\text{Se}_{\underline{x}}\text{S}_{1-\underline{x}}$ .  
 Department of Physics, Faculty of Science, Niigata University. PHYSICAL SOCIETY OF JAPAN, JOURNAL v. 15, p. 1586-1595, Sep 1960.

The electrical properties such as the electronic and ionic conductivities, Hall coefficients, etc., of the alloys Ag<sub>2</sub>(Te, Se; Te, S; Se, S) are studied with use of the galvanic cell Ag | AgI | specimen | Pt, the excess Ag content being controlled by sending a current across the cell. The electrical properties of these alloy systems change continuously in the  $\alpha$  phase as the mixing ratio x is varied, while they change discontinuously or rapidly at certain x's in the  $\beta$  phase. The experimental results are compared with theory under simplifying assumptions such as the energy-independent relaxation time and the energy-momentum relation given by  $\mathcal{E} = \frac{\hbar^2 k^2}{2m} (1 - \frac{Bk^2}{B_0})$ .

37. Miyatani, Shinya  
 Infrared absorption of  $\alpha\text{-Ag}_2\text{Te}_{\underline{x}}\text{S}_{1-\underline{x}}$ .  
 University of Niigata. PHYSICAL SOCIETY OF JAPAN, JOURNAL v. 14, p. 1634, 1959.

The experimental specimen had an x value of 0.7. It was rolled into foil sufficiently thin to give large interference effects in infrared transmission. Electrical conductivities were determined in the galvanic cell (Ag | AgI+5% AgCl | specimen | Pt). The curves of absorption coefficient vs. wave number were obtained for various electrical conductivities. The spectral range was 1000 to 2500 cm<sup>-1</sup>. The absorption coefficient varied between  $10^{-2}$  and  $4 \times 10^{-3}$ , and had minimum between 1100 and 1500 cm<sup>-1</sup>. Free-electron absorption was dominant at the longer wavelengths. The relaxation time, if assumed to be energy-independent, was  $6.6 \times 10^{-14}$  sec. The Drude-Zener formula gave  $5.4 \times 10^{-14}$  sec., which is considered to be in good agreement.

38. Murphy, M. J.  
 AN X-RAY STUDY OF SOME MINERAL  
 SULFO-SALTS. M.S. Thesis, University  
 of California at Berkeley, 1953.

39. Niizeki, N.  
 STRUCTURAL STUDIES OF THE MINERAL  
 SULPHO-SALTS. Ph.D. Thesis,  
 Massachusetts Institute of Technology, 1957.

40. Nitsche, R. and Merz, W. J.  
 Photoconduction in ternary V-VI-VII  
 compounds. J. PHYS. CHEM. SOLIDS  
 v. 13, n. 1-2, p 154-5, May 1960.  
 Some photoelectric properties of single crystals of ternary compounds of the type V-VI-VII (V = Sb, Bi; VI = S, Se, Te; VII = Cl, Br, I) were studied. The wavelengths of maximum photocurrent,  $\lambda_{max}$ , shift in a regular way towards longer wavelengths with increasing atomic weight of the components. For the compounds SbSBr and SbSI the dependence of photocurrent, dark current and  $\lambda_{max}$  on temperature was measured between -140 and +120° C.

41. Palatnik, L. S., et al  
 A group of ternary semiconducting compounds.  
 SOVIET PHYSICS - DOKLADY v. 6, n. 3,  
 p. 241-43, Sep 1961.  
 A method for development of additional ternary semiconducting compounds is presented. In this method the crystal-geometric criterion which determines whether the original coordinational configuration is retained in the compounds obtained must be taken into account as well as the chemical bond. Thus for the compounds  $Cu_2PbS_3$ ,  $Cu_2PbSe_3$ , and others, the chemical means of selection of semiconducting compounds and Goodman's method of "cross-" and "vertical" substitution of elements turns out unsuitable insofar as these compounds, being thermodynamically unstable, are not actually realized.

42. Ramdohr, P. and Schmitt, M.  
 Oregonit, ein neues Nickel-Eisenarsenid mit metallartigen

42. (cont'd)

Eigenschaften. NEUES JAHRBUCH  
FUER MINERALOGIE, MONATSCHRIFTEN  
n. 11-12, p. 239-47, 1959. (In German)

The mineral occurs as water-rolled pebbles in Josephine Creek, Oregon; the pebbles have a smooth brown crust. X-ray fluorescence analysis (data not given) corresponds to  $\text{Ni}_{10}\text{Fe}_6\text{As}_9$  or  $\text{Ni}_2\text{FeAs}_2$ . A little Co and some traces of Cu are present. Oregonite is hexagonal,  $a = 6.083 \pm 0.003$ ,  $c_0 = 7.130 \pm 0.005$ ,  $c/a = 1.1732$ ,  $Z=3(\text{Ni}_2\text{FeAs}_2)$ ,  $G = 6.92$ .

43.

Rodot, H.  
Study of the properties of the system  
 $\text{AgSbTe}_2$ - $\text{PbTe}$ . C. R. ACAD. SCI.  
(PARIS) v. 249, n. 19, p. 1872-4, 9 Nov 1959.  
(In French)

Up to 40% PbTe, the alloys are solid solutions of cubic structure (NaC type). For higher proportions two phases exist. For the solid solutions the lattice spacing is greater than for pure  $\text{AgSbTe}_2$  and the melting points are lower. The electrical properties are investigated and the potentialities of the materials for thermoelectric devices are discussed.

44.

Semiletov, S. A. and Man, L. I.  
Study of the structure of  $\text{TlBiSe}_2$  and  
 $\text{TlSbS}_2$  in thin films by the electron  
diffraction method. Crystallographical  
Institute of the Academy of Sciences of the  
USSR. KRISTALLOGRAFIYA v. 4, n. 3,  
p. 414-417, 1959. (In Russian)

The authors studied the structure of the two compounds in a manner similar to that of Pinsker, Z. G., Semiletov, S. A., and Belov, Ye. N., in studying the structure of  $\text{TlSbSe}_2$ . The latter substance was discovered by Kolomiyets, B. T., and Goryunova, N. A., while they investigated the electric properties of the semiconducting  $\text{Tl}_2\text{S-Sb}_2\text{S}_3$  isomorphous series. The authors sublimated thin films of  $\text{TlBiSe}_2$  and  $\text{TlSbS}_2$  upon NaCl crystals or celluloid and let the films crystallize by annealing; in the case of a rapid sublimation, the films were readily crystalline. They obtained two kinds of electron diffraction patterns of  $\text{TlBiSe}_2$ : (1) a few diffuse lines; (2) numerous sharp lines, of which the most intensive ones corresponded to the lines of the powder photographs of the same substance. Only the former pattern could be interpreted. The latter pattern indicates the presence of another modification whose structure is still unknown. The unit cell of the identified modification is face-centered cubic;  $a = 6.18 \pm 0.02$  Å; volume of the unit cell = 238 Å<sup>3</sup>; density = 8.25; there are two formula molecules per unit cell; Tl and Bi atoms occupy available positions statistically. The unit cell of

44. (cont'd) Tl SbS<sub>2</sub> is also face-centered cubic; a varies from 5.87 to 5.94 Å because of slight variations in the composition. Harker diagrams point to the similarity of the structures of both compounds to that of NaCl. Both of these compounds, as well as some other trinary compounds studied by other authors, prove the existence of numerous semiconducting crystalline substances of similar compositions and of structure similar to that of NaCl. The generalized formula of these compounds is A<sub>1</sub>B<sub>1</sub>X<sub>2</sub><sup>V</sup><sub>VI</sub>, where A stands for a one valence element; B for a five valence element; and X<sub>2</sub><sup>V</sup><sub>VI</sub> for a six valence element, such as S, Se, Te. Some of these compounds are likely to occur only in the form of orthorhombic modifications, like TlSbSe<sub>2</sub>, but the others also in cubic crystals of NaCl type.

45. Shtrum, E. L.  
 Semiconducting properties of the AgFeTe<sub>2</sub> phase. FIZ. TVERDOGO TELA v. 2, n. 7, p. 1489-93, July 1960. (In Russian)  
 Metallographic and X-ray diffraction studies showed that AgFeTe<sub>2</sub> undergoes two phase transitions (at 150 and 520°C) and that it is single-phased within a range of compositions departing up to 4 at. % from stoichiometry. Within this range the compound is a semiconductor, as shown by measurements of its electrical conductivity and thermoelectric power.

46. Talybov, A. G.  
 Electron diffraction study of the structure of SnSb<sub>2</sub>Te<sub>4</sub>. SOVIET PHYSICS -- CRYSTALLOGRAPHY v. 6, n. 1, p. 40-44, July-Aug 1961.  
 The results of an electron diffraction study of the structure of SnSb<sub>2</sub>Te<sub>4</sub> are presented.

47. Thompson, R. M.  
 DESCRIPTIVE MINERALOGY OF THE TELLURIDES. Ph.D. Thesis, University of Toronto, 1947, 257p.  
 Among the tellurides described, such ternary minerals as pelzite, sylvanite, nagyagite, and tetradyomite are included.

48. Tischendorf, G.  
 Ueber Eskebornit von Tilkerodl im Harz.  
 NEUES JAHRBUCH FUER MINERALOGIE

48. (cont'd)

ABHANDLUNGEN v. 94, p. 1169-82,  
1960. (In German)

The formula of eskebornite has been given as FeSe and  $\text{Fe}_3\text{CuSe}_4$ . Two analyses of synthetic preparations with a 5.53-5.55 Å. (for natural material a 5.53<sub>5</sub> Å.) gave  $\text{Cu}_{0.43}\text{Fe}_{0.61}\text{Se}$  and  $\text{Cu}_{0.55}\text{Fe}_{0.62}\text{Se}$ , and an X-ray fluorescence analysis of another synthetic preparation gave  $\text{Cu}_{0.55}\text{Fe}_{0.55}\text{Se}$ . The general formula may be  $(\text{Cu}, \text{Fe})_{1.1}\text{Se}$ . X-ray powder data are given.

49.

Uphoff, H. L. and Healy, J. H.  
Semiconducting properties of inorganic  
amorphous materials. J. APPL. PHYS.  
(USA) v. 32, n. 5, p. 950-4, May 1961.

Ten compositions were prepared in the systems As-Se-Te and As-S-Te. Nine of these compositions were amorphous in structure. The resistivities and Seebeck coefficients of these materials were measured as functions of temperature. The resistivity varied exponentially with temperature, while the Seebeck coefficient varied linearly. At 298°K, the resistivity values for the amorphous samples ranged from  $4.7 \times 10^4$  to  $2.5 \times 10^{13}$  ohm cm, while the Seebeck coefficient values ranged from 830-1625  $\mu$  V deg<sup>-1</sup> K (p type). At any temperature, the resistivity decreased with increase in tellurium content. For the amorphous materials, the thermal conductivity values ranged from 2.4 to 4.4 mW cm<sup>-1</sup> deg<sup>-1</sup> K.

50.

Vul'f, V. K.  
Ternary metal compounds. USPEKHI  
KHIMII v. 29, n. 6, p. 774-85, 1960.  
(Translated by Aerospace Technical  
Intelligence Center, Wright-Patterson  
Air Force Base, Trans. no. MCL-724,  
13 Feb 61, 50p.)

Contents: General features of ternary metal compounds; Ternary Kurnakov phases; Valent ternary metal compounds; Electronic ternary metal compounds; Ternary Laves phases; Ternary Ni-arsenide phases; Ternary interstitial phases; Properties and practical application of ternary metal compounds. A bibliography of 174 references is appended.

51.

Wachtel, A.  
(Zn, Hg)S and (Zn, Cd, Hg)S  
electroluminescent phosphors. Westinghouse.

51. (cont'd) J. ELECTROCHEM. SOC. v. 107,  
p. 682-688, Aug 1960.

Solid solutions of (Zn, Hg)S prepared by firing in sealed silica tubes are discussed. The crystals are cubic in structure. With suitable additions of Cu and a coactivator, e.g. halides, Ga, or In, photoluminescence and electroluminescence are obtained. The electroluminescence in the red consists of two emission bands which do not appear to be analogous to the blue and green emission bands of Cu, Cl in ZnS. The quantum efficiency is of the same order of magnitude as that of ZnS:Cu, Cl, but the emission bandwidth is about twice as large and the red electroluminescence consists of emission located to a large extent in the infrared. HgS tends to retain the cubic structure of ternary (Zn, Cd, Hg)S systems provided the Cd/Hg ratio does not exceed certain limits; until this is so, the introduction of Cd causes increased electroluminescence.

52. Wernick, J. H., Geller, S. and Benson, K. E.  
Constitution of the  $\text{AgSbSe}_2$ - $\text{AgSbTe}_2$ - $\text{AgBiTe}_2$   
system. J. PHYS. CHEM. SOLIDS v. 7, n. 2-3,  
p. 240-8, Nov 1958.

The six pseudo-binary phase diagrams in the semiconducting system  $\text{AgSbSe}_2$ - $\text{AgSbTe}_2$ - $\text{AgBiSe}_2$ - $\text{AgBiTe}_2$  have been determined. Complete series of solid solutions with the cubic structure exist in this pseudo-quaternary system. The locus of temperatures and compositions for the order-disorder transition has been determined. Lattice constants as a function of composition for the cubic phase and thermoelectric-power data for some of the solid solutions are presented.

53. Wernick, J. H.  
Constitution of the  $\text{AgSbS}_2$ -PbS,  $\text{AgBiS}_2$ -PbS,  
and  $\text{AgBiS}_2$ - $\text{AgBiSe}_2$  systems. AMERICAN  
MINERALOGIST v. 45, n. 5-6, p. 591-98,  
May-June 1960.

Complete series of solid solutions with the disordered NaCl-type structure exist in the pseudo-binary  $\text{AgSbS}_2$ -PbS and  $\text{AgBiS}_2$ -PbS systems. Thus, synthetic compositions corresponding to the minerals freieslebenite and diaphorite in the  $\text{AgSbS}_2$ -PbS system have high temperature forms with the disordered NaCl structure. Only this cubic form was obtained for the composition corresponding to the mineral schermirite in the  $\text{AgBiS}_2$ -PbS system. Lattice constants as a function of composition for the cubic phase are presented. The high and low temperature modifications of  $\text{AgBiS}_2$  and  $\text{AgBiSe}_2$  form a complete series of solid solutions. The phase diagram for this system has been determined. Lattice constants as a function of composition for the cubic phase follow Vegard's law, and this is presumed to be the case for the low temperature form.

54.

Wernick, J. H.

Metallurgy of some ternary semiconductors  
 and constitution of the  $\text{AgSbSe}_2$ - $\text{AgSbTe}_2$ -  
 $\text{AgBiSe}_2$ - $\text{PbSe}$ - $\text{PbTe}$  System. Bell Telephone  
 Laboratories, Inc., Murray Hill, New Jersey.  
 Paper from "Properties of Elemental and  
 Compound Semiconductors. METALLURGICAL  
 SOCIETY CONFERENCES v. 5, p. 69-88, 1960.  
 Interscience Publishers, New York.  
 (QC612.S4 Am35.7p)

Metallurgical techniques employed in the preparation of some semiconducting ternary compounds are discussed. Some electrical and thermal properties are presented. In addition, six pseudo-binary phase diagrams in the semiconducting pseudo-quinary system,  $\text{AgSbSe}_2$ - $\text{AgSbTe}_2$ - $\text{AgBiSe}_2$ - $\text{PbSe}$ - $\text{PbTe}$ , have been determined. A complete series of solid solutions with the disordered  $\text{NaCl}$ -type structure exists in this system. The locus of temperatures and compositions for the order-disorder transition has been determined. Lattice constants as a function of composition for the cubic phase are also presented. The valence electron to atom ratio increases from 4-1/2 to 5 in going from the ternary to the binary compound, and large negative deviations from Vegard's law occur in all but the  $\text{AgSbTe}_2$ - $\text{PbSe}$  system. A positive deviation occurs in the  $\text{AgSbTe}_2$ - $\text{PbSe}$  system. Possible reasons for these deviations are discussed.

55.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
 DEVICES MADE THEREFROM. U.S.  
 PATENT 2,882,192, 14 Apr 59, assigned  
 to Bell Telephone Laboratories, Inc.

Ternary semiconducting compounds are synthesized which have energy gaps of about 0.8 e.v.  $\text{Cu}_3\text{SbS}_4$ , melting at 555°, energy gap 0.8 e.v., and  $\text{Cu}_3\text{AsS}_4$ , melting at 655°, energy gap 0.8 e.v., are made by mixing the respective components in a C-coated  $\text{SiO}_2$  crucible which is placed inside a second  $\text{SiO}_2$  container. This container is evacuated and filled with N, and then sealed off. It is placed in the electric furnace which is wound so that there are three heating zones capable of operating independently. During 3 hours the middle zone heats the crucible to about 680°, while the two ends are maintained about 100° higher. This condition is maintained for 2 hours, then the lower zone of the furnace is shut off, creating a gradient of about 700° to 450°, which is held for 1 hour. Finally, all zones are shut off and the system is allowed to cool to room temperature. A device utilizing either of the materials can be made using 0.01 at. % I as the significant impurity.

56.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U.S.

PATENT 2,882,193, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

P-N junction devices having intrinsic energy gaps of from 0.8 to 2.0 e.v. are made by the addition of impurities from Group VII to the substances  $\text{Cu}_3\text{SbS}_3$ ,  $\text{Ag}_3\text{AsS}_3$ , and  $\text{Cu}_3\text{AsS}_3$ . The process is similar to that described in the preceding abstract.

57.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U.S.

PATENT 2,882,194, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

Describes the means of producing p-n junction devices by the addition of iodine to the substances  $\text{CuSbS}_2$  and  $\text{AgBiS}_2$ .

58.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U.S.

PATENT 2,882,195, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

P-N junction devices having intrinsic energy gaps of 0.7 to 0.9 e.v. are produced by introducing group VII impurities into the substances  $\text{CuPbSbS}_3$ ,  $\text{CuPbAsS}_3$  and  $\text{CuPbBiS}_3$ .

59.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U.S.

59. (cont'd)

PATENT 2,882,467, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

$\text{AgSbSe}_2$ , melting at  $610^\circ$ , energy gap 0.6 e.v., exhibits p-type conductivity, and after passage of 20 zones in a zone-refining process, has a resistivity of 0.02 ohm-cm.  $\text{AgBiSe}_2$ , melting at  $780^\circ$ , exhibits n-type conductivity.  $\text{AgAsSe}_2$ , melting at  $390^\circ$ , has an energy gap of 0.9 e.v. A Device, either point-contact or junction, in which the significant impurity is up to 0.01 at. % I, (Mn, Zn, or Cd) can be made using these compounds.

60.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U.S.

PATENT 2,882,468, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

$\text{AgXTe}_2$ , in which X is Sb, Bi, or As is made by a similar procedure, except that the furnace is heated during 4 hours to  $1000^\circ$ , and the end zones are maintained  $100^\circ$  higher.  $\text{AgSbTe}_2$ , melting at  $555^\circ$ , energy gap 0.7 e.v., and exhibits p-type conductivity,  $\text{AgBiTe}_2$ , melting at  $510^\circ$ , energy gap 0.3 e.v., exhibits n-type conductivity.  $\text{AgAsTe}_2$ , melts at  $325^\circ$ , energy gap 0.8 e.v., exhibits p-type conductivity. A device, either point-contact or junction in which the significant impurity is up to 0.01 at. % I, can be made with any of these materials.

61.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND DEVICES  
MADE THEREFROM. U.S. PATENT 2,882,  
469, 14 Apr 59, assigned to Bell Telephone  
Laboratories, Inc.

$\text{CuSbSe}_2$  and  $\text{CuAsSe}_2$  are made according to the procedure described in U.S. Patent 2,882,468 at  $1000^\circ$  and  $\text{CuAsS}_2$  is made at  $700^\circ$ .  $\text{CuSbSe}_2$  melting at  $460^\circ$ , has an energy gap of 0.6 e.v.  $\text{CuAsSe}_2$  melting at  $415^\circ$ , has an energy gap of 0.4 e.v.  $\text{CuAsS}_2$  melting at  $625^\circ$ , has an energy gap of 0.8 e.v. All exhibit p-type conductivity. A device in which the significant impurity is up to 0.01 at. % I, can be made use of these compounds.

62.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U. S.

PATENT 2,882,470, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

$\text{Cu}_3\text{SbSe}_4$  is made according to the procedure described in the previous patent (2,882,469) at  $1000^\circ$ . However, for preparation of this material, the inner crucible must be first coated by exposure to a mixture of 4 parts N and 1 part  $\text{CH}_4$  for 15 minutes at a flow rate of 250 cc./min. with the crucible at  $1000^\circ$ .  $\text{Cu}_3\text{SbSe}_4$ , melting at  $425^\circ$ , has an energy gap of 0.2 e.v., and exhibits p-type conductivity.

63.

Wernick, J. H.

SEMICONDUCTING MATERIALS AND  
DEVICES MADE THEREFROM. U. S.

PATENT 2,882,471, 14 Apr 59, assigned  
to Bell Telephone Laboratories, Inc.

$\text{Ag}_3\text{AsSe}_3$ , made as described in the previous patent (2,882,470), melts at  $385^\circ$ , has an energy gap of 0.4 e.v., and exhibits n-type conductivity. A device in which conversion is caused by alloying with Ge containing Ga as the significant impurity, can be made with this compound.

64.

Wiese, J. R. and Muldawer, L.

Lattice constants of  $\text{Bi}_2\text{Te}_3$ - $\text{Bi}_2\text{Se}_3$   
solid solution alloys. Franklin Inst.

Labs. J. PHYS. CHEM. SOLIDS v. 15,  
p. 13-16, Aug 1960.

The  $\text{Bi}_2\text{Te}_3$ - $\text{Bi}_2\text{Se}_3$  quasi-binary system is rhombohedral for all compositions. Lattice constants  $a_0$  and  $c_0$  (based on a hexagonal lattice) for the entire range determined using powder pattern film techniques are reported. The constant  $a_0$  follows Vegard's rule over the entire range of compositions, while the constant  $c_0$  exhibits a positive deviation over the range from 40 mol.-%  $\text{Bi}_2\text{Te}_3$  to  $\text{Bi}_2\text{Se}_3$ .  $\text{Bi}_2\text{Te}_3$  has a layered structure with planes of atoms of a single type parallel to the basal plane. The lattice constant data can be explained in terms of Se-atom substitution in preferred planes

64. (cont'd) for the range  $\text{Bi}_2\text{Te}_3$ - $\text{Bi}_2\text{Te}_2\text{Se}$ . Interlayer spacings for  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_2\text{S}$  are given and discussed.

65. Wolfe, R., Wernick, J. H. and Haszko, S. E.  
 Anomalous Hall effect in  $\text{AgSbTe}_2$ .  
 J. APPL. PHYS. v. 31, n. 11,  
 p. 1959-64, Nov 1960.

The Hall coefficient of the ternary semiconductor  $\text{AgSbTe}_2$  near room temperature is positive in some specimens and negative in others, although the Seebeck coefficient is always positive. The negative Hall coefficient decreases as the temperature is lowered from  $180^\circ\text{K}$  to  $70^\circ\text{K}$  and changes sign in lower temperatures. This negative Hall coefficient is associated with the presence in the  $\text{AgSbTe}_2$  of a second phase consisting of  $\text{Ag}_2\text{Te}$ . The properties of the two-phase material are interpreted in terms of the theory of the transport properties of inhomogeneous semiconductors. In single-phase  $\text{AgSbTe}_2$  containing  $3 \times 10^{19}$  holes per  $\text{cm}^3$ , the hole mobility is  $35 \text{ cm}^2/\text{V sec}$  at  $300^\circ\text{K}$  and it varies approximately as  $T^{-0.5}$ . (It has been suggested by Armstrong, Faust, and Tiller (Abstract 2, page 1) that the microstructure is associated with the presence of  $\text{Sb}_2\text{Te}_3$  as a Widmanstatten precipitate along {111} planes in the  $\text{AgSbTe}_2$ . This would indicate that none of the material was single phase. Even though the  $\text{Sb}_2\text{Te}_3$  in the measured specimens is present in quantities too small to be detected in the present X-ray powder photographs, it may have some effect on the measured properties. Therefore, the electrical properties of single phase  $\text{AgSbTe}_2$  have yet, to be determined). The lattice thermal conductivity is so low ( $0.0064 \text{ W cm}^{-1} \text{ deg}^{-1}$  C at  $290^\circ\text{K}$ ) that the calculated "phonon mean free path" is less than the nearest neighbor distance. The thermal conductivity of a specimen rich in  $\text{AgSbTe}_2$ - $\text{Ag}_2\text{Te}$  eutectic is higher than that of either of the components. This excess thermal conductivity is attributed to circulating thermoelectric currents.

66. Woolley, J. C. and Ray, B.  
 Solid solution in  $A^{II}B^{VI}$  tellurides.  
 Dept. of Physics, Univ. of Nottingham,  
 England. PHYSICS AND CHEMISTRY OF  
 SOLIDS v. 13, nos. 1-2, p. 151-53, May 1960.

Alloys have been produced for the three systems  $\text{CdTe}-\text{HgTe}$ ,  $\text{CdTe}-\text{ZnTe}$  and  $\text{HgTe}-\text{ZnTe}$  and annealed to obtain equilibrium conditions. It has been confirmed that solid solution occurs at all compositions in each system and the variation of lattice parameter with composition has been determined in each case. The form of the solidus curve has been obtained by X-ray methods in the  $\text{HgTe}-\text{ZnTe}$  system.

67. Yelagina, Ye. I. and Abrikosov, N. Kh.  
 An investigation of the systems PbTe-Bi<sub>2</sub>Te<sub>3</sub>  
 and SnTe-Sb<sub>2</sub>Te<sub>3</sub>. (Issledovaniye sistem  
PbTe-Bi<sub>2</sub>Te<sub>3</sub> i SnTe-Sb<sub>2</sub>Te<sub>3</sub>). ZHURNAL  
 NEORGANICHESKOI KHIMII v. 4, n. 7,  
 p. 1638-42, 1959. (In Russian)

The present investigation was carried out with the intention of finding new semiconductors. No published data are available on the ternary system Pb-Bi-Te. The system Sn-Sb-Te has not been examined. In the alloys produced, microstructure was investigated, and the thermoelectromotive force referred to Cu at a temperature difference of 20 C, as well as electric conductivity were measured. In the first mentioned system, the primary crystallizing phase consists of PbTe. With increasing Bi<sub>2</sub>Te<sub>3</sub> content, the crystallization temperature drops, until, finally, at 82.7% Bi<sub>2</sub>Te<sub>3</sub>, a single-phase coarse-crystalline structure is formed, which corresponds to the compound PbTe-2Bi<sub>2</sub>Te<sub>3</sub> and which is located in the phase diagram on the ordinate passing through the inflection of the solidus curve. X-ray analyses confirm the existence of the ternary intermediate phase. At 71.8% Sb<sub>2</sub>Te<sub>3</sub> the compound SnTe-Sb<sub>2</sub>Te<sub>3</sub> is formed.

68. Yelagina, Ye. I. and Abrikosov, N. Kh.  
 The PbTe-Bi<sub>2</sub>Te<sub>3</sub> and SnTe-Sb<sub>2</sub>Te<sub>3</sub>  
 systems. ZHURNAL NEORGANICHESKOI  
 KHIMII v. 4, p. 1638-42, 1959. (In  
 Russian)

A study of the phase diagrams of the ternary systems Pb-Bi-Te and Sn-Sb-Te along the PbTe-Bi<sub>2</sub>Te<sub>3</sub> and SnTe-Sb<sub>2</sub>Te<sub>3</sub> cross sections showed the existence of the ternary compounds PbTe<sub>3</sub>•2Bi<sub>2</sub>Te<sub>3</sub> and SnTe-Sb<sub>2</sub>Te<sub>3</sub> which melt congruently.

69. Zalar, S. and Cadoff, I.  
 A STUDY OF A CLASS OF INTER-  
 METALLIC COMPOUNDS, THE  
 CHALCOPYRITES. New York Univ.,  
 Coll. of Engineering, N. Y. Rept. for

69. (cont'd)                   Feb 57 - Aug 60; ARL TR 60-316,  
                                  Oct 60, 54p. (Contract AF33(616)  
                                  3959, Proj. 7021) ASTIA AD-252 808

Three compositions of the class of polyatomic semiconductors of the chalcopyrite structure A (I) B (III)C<sub>2</sub> (6+) were investigated by thermal, microscopic, mechanical and electronic methods. Only the first two were found to be intermetallic semiconductors, the composition AuInTe<sub>2</sub> showing the metallic character of a two phase alloy, Au.25In.25Te.50. Melting points, Vickers hardness, micro and macrostructures of CuInTe<sub>2</sub>, AgInTe<sub>2</sub>, and Au.25In.25Te.50 were determined. At room temperature the electrical resistivity of CuInTe<sub>2</sub> was of the order of 1/100 ohm-cm, that of AgInTe<sub>2</sub> of the order of 1-10 ohm-cm and that of Au.25In.25Te.50 of the order of 1/10,000 ohm-cm.

70.                           Zhuze, V. P., Sergeeva, V. N. and Shtrum, E. L.  
                                  Semiconducting compounds with the general  
                                  formula ABX<sub>2</sub>. ZH. TEKH. FIZ. v. 28, n. 10,  
                                  p. 2093-108, 1958. (In Russian)

A survey of some 25 compounds in two groups: (1) chalcopyrite and related structures for which A is Cu or Ag, B is Al, Ga, In, Ti or Fe, X is S, Se, Te; (2) derived NaCl and other structures for which A is Cu or Ag, B is Sb or Bi, X is Se or Te. Data are given for most of these compounds, on electrical and other physical properties (e.g. melting point, electrical conductivity). Chemical bonding is discussed for the first group. It is also noted that X-ray powder diagrams for CuBiTe<sub>2</sub>, AgBiTe<sub>2</sub> and CuSbTe<sub>2</sub> appear similar in type to those for Bi<sub>2</sub>Te<sub>3</sub>.

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